

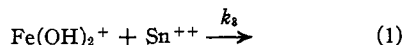
In conclusion I wish to express my gratitude to Professor William C. Bray for his advice and suggestions during the progress of the work.

Summary

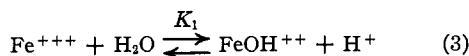
Rate measurements are presented for the reaction between ferric and stannous perchlorates in solutions containing perchloric acid at 70 and 55°. The rate is much slower than when chloride ion is present.

There is no evidence for a direct reaction between ferric ion and stannous ion. The failure of the two ions to react at an appreciable rate is attributed to the high repulsive forces between these polyvalent, positive ions.

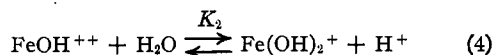
The experimental results are in agreement with the theory that the rate determining step for the reduction of the ferric salt is



When the hydrolysis equilibria



and



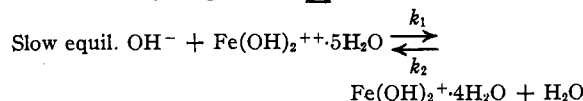
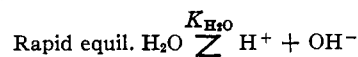
are maintained the rate law is

$$d(\text{Fe}^{++})/dt = 2k_3K_1K_2(\text{Fe}^{+++})(\text{Sn}^{++})/(\text{H}^+)^2 \quad (2)$$

This law represents the initial rate in all experi-

ments and applies throughout when the concentration of ferric ion is high compared to that of stannous ion. The specific rate, $2k_3K_1K_2$, is 660×10^{-4} at 70° and 26.2×10^{-4} at 55°.

A study of the deviations from equation 2 led to the conclusions that reaction 4 is not rapid compared to Reaction 1 and that the mechanism of reaction 4 is



The study resulted in the determination of the product, K_1K_2 , at 70° and the ratio, k_3/k_2 at 70° and 55°. Combination with the value of the specific rate, $2k_3K_1K_2$, gave the following values at 70°: $K_1K_2 = 35.2 \times 10^{-4}$, $k_3 = 9.4$ and $k_2 = 0.162$.

While neither of the hydrolysis quotients, K_1 nor K_2 , has been determined directly, values of each have been chosen which are consistent with the above results and with available data for the hydrolysis of ferric ion. The resulting values of the various equilibrium quotients and specific rates at 70 and 55° are listed in Table VII. Concentrations are expressed in moles per liter and time intervals in minutes.

BERKELEY, CALIF.

RECEIVED JULY 10, 1936

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

The Activation of Specific Bonds in Complex Molecules at Catalytic Surfaces. II. The Carbon-Hydrogen and Carbon-Carbon Bonds in Ethane and Ethane-*d*

BY KIYOSHI MORIKAWA,¹ W. S. BENEDICT AND HUGH S. TAYLOR

The activation of the carbon-hydrogen and carbon-carbon bonds in ethane at nickel catalyst surfaces can be studied with the aid of deuterium since two reactions may be examined: (a) the exchange reaction which may be generalized as $\text{C}_2\text{H}_x\text{D}_y + \text{D}_2 = \text{C}_2\text{H}_{x-1}\text{D}_{y+1} + \text{HD}$ in which $x + y = 6$ and y may have any integral values from 0 to 5; and (b) the methane producing reaction $\text{C}_2\text{H}_6 + \text{H}_2 = 2\text{CH}_4$. The former reaction involves the C-H bond, the latter the C-C bond. Deuterium permits these reactions to be studied when they are occurring simultaneously on a given catalyst under given conditions of temperature

(1) Visiting research fellow of the South Manchuria Railway Co., Dairen, Japan.

and pressure. During the course of this work, also, investigation was made of the kinetics of methane formation from ethane and hydrogen, the data providing interesting aspects of the mechanism of activation of the ethane at nickel surfaces.

Experimental Details

Materials.—Electrolytic hydrogen and deuterium from the electrolysis of ordinary and heavy water ($d^{2\text{H}_2} = 1.1079$) were employed. Ethane was produced catalytically from ethylene and hydrogen over a nickel catalyst at room temperature. It was purified by combustion of the excess hydrogen over copper-copper oxide, followed by fractional distillation to remove nitrogen and methane present.

The comparison of exchange reaction and methane formation was conducted by a dynamic method in which the gas mixtures $C_2H_6 + D_2(H_2)$ were slowly passed backward and forward over a nickel catalyst supported on kieselguhr. Vapor baths were employed for temperature control. The catalyst was similar to that described in Part I of this series,² and was protected against mercury vapor by two traps at -78° . The kinetic studies were made in a static system.

Analytical Procedure.—The progress of the exchange reaction was again followed by infra-red absorption measurements of the C-H and C-D bonds as already described.^{2,3} The formation of methane was followed by combustion of the hydrogen over copper-copper oxide at 300° . From the data thus obtained, the volume of hydrogen consumed in the reaction could be checked against the increase in hydrocarbon volume. This double check was occasionally further confirmed by fractional extraction of methane from ethane at liquid air temperature. The accuracy attainable may be illustrated by expt. 27. In this experiment 19.6 cc. of C_2H_6 and 20.4 cc. of H_2 were treated for one hour in contact with 2.0 g. of nickel catalyst at 184° to give a final volume of 39.7 and 26.2 cc. of residual hydrocarbon. Calculating from the hydrogen decrease 13.8 cc. of CH_4 was formed. From the hydrocarbon increase 13.2 cc. was formed. Fractionation of the residual hydrocarbon gave >12.1 cc. of methane and <14.1 cc. of ethane, the latter certainly still containing some dissolved methane. It was found that methane dissolved readily in and was persistently retained by the condensed higher hydrocarbon. The larger the methane content the easier and more accurate was the fractionation.

Experimental Results

Comparison of Exchange Reaction and Methane Formation.—The data of Tables I and II represent the measurements made by the dynamic method to effect this comparison, the same nickel catalyst, 2.5 g., being used for both sets of data.

TABLE I
THE REACTION $C_2H_6 + H_2 = 2CH_4$

Expt.	C_2H_6 , cc.	H_2 , cc.	Temp., $^\circ C.$	Time, hrs.	Conversion % C_2H_6 reacted
4	20.9	21.0	110	1	0
11	25.9	28.5	157	3	11.9
9	24.8	26.4	172	1	19.3
10	22.9	25.4	184	1	92
5	21.8	22.5	184	1	73.2
2	22.4	22.5	302	1	100

These results show that the exchange reaction becomes, under the given conditions, quite marked already at 110° whereas methane formation only becomes appreciable around 150° and is fast at 180° . There is therefore about 60° difference in

(2) Morikawa, Benedict and Taylor, *THIS JOURNAL*, **58**, 1445 (1936).

(3) Benedict, Morikawa, Barnes and Taylor, *J. Chem. Phys.*, forthcoming publication.

TABLE II
THE EXCHANGE REACTION $C_2H_6D_v + D_2 = C_2H_{z-1}D_{v+1} + HD$

Expt.	C_2H_6 , cc.	D_2 , cc.	Temp., $^\circ C.$	Time, hrs.	C-D Bond % equilibrium
12	22.1	44.4	25	22	0
13	21.4	43.1	110	2.5	33
8	25.6	52.3	138	2.5	100
7	22.7	41.5	302		0 ^a

^a This experiment was conducted in presence of Cu-CuO at 302° to show that the hydrogen removal during analysis did not effect exchange.

temperature, on this catalyst, between comparable activations of the C-H and C-C bonds in ethane. The data of Table II also suggested the following method of preparation of C_2D_6 .

Preparation of Ethane- d_6 .—Two grams of nickel catalyst was reduced at 450° for five and a half hours and then evacuated for two hours. At 0° , 22.2 cc. of C_2H_4 and 50.4 cc. of D_2 were introduced to the catalyst and when hydrogenation was complete the temperature was raised to 138° and there maintained for two and a half hours. The hydrogen-deuterium was then removed by combustion at 275° and next the partially deuterized ethane was subjected to the same procedure, each time with twice its volume of pure deuterium, for seven successive treatments. If the equilibrium constant is approximately 1 and the equilibrium is established in each treatment the final ethane should have been $\sim 99\%$ C-D. This was actually found to be the case by infra-red measurements. The recovered C_2D_6 had a volume of 22 cc. and the methane formed throughout the experiment was 0.27 cc. The C_2D_6 had a negligible vapor pressure at liquid air temperatures. We shall report elsewhere some of the physical properties of this product.

The Kinetics of the Reaction $C_2H_6 + H_2 = 2CH_4$.—The data of Table III record the results of static experiments on 1 g. of nickel catalyst at 172 and 184° in a reaction space of 125 cc. with 3 cc. dead space for the dry ice traps. The experiments were so conducted that, at each stage, the hydrogen, removed by combustion for analytical purposes, was replaced by an equal volume of hydrogen and the next stage followed. The data are all recorded as pressures of gas in mm. at a constant volume of 88 cc. corrected to 25° .

Comparison of expts. 2a and 3 indicates that the activity of the catalyst is constant and that the trend upward in conversion per hour as the re-

TABLE III
 THE REACTION $1C_2H_6 + 1H_2 = 2CH_4$

Expt.	Temp., °C.	Initial pressure, mm.				Time inter- val, hrs.	Final pressure, mm.				$-\Delta P_{C_2H_6}$ % per hr.
		Total	C_2H_6	H_2	CH_4		Total	H.C.	$+\Delta H.C.$	$-\Delta H_2$	
1a	172	349.6	174.4	175.2	0	0-1.5	345.7	182.0	7.6	11.5	2.9
b	172	364.3	166.8	182.4	15.2	1.5-3	364.1	189.0	7.0	7.3	2.7
c	172	355.5	159.8	166.5	29.2	3-6.2	355.1	202.1	13.1	13.5	2.4
d	172	355.1	136.7	152.9	75.4	6.2-	355.7	250.4	48.3	47.6	2.8
						16.2-					
e	172	353.8	98.4	103.4	152.0	16.2-	352.5	263.3	12.9	14.2	3.7
						18.2-					
f	172	354.5	84.8	91.1	179.2	18.2-	353.9	281.6	18.3	18.8	4.2
						20.7					
2a	184	352.3	175.5	176.8	0	0-1	351.5	193.5	18.0	18.8	10.3
b	184	351.8	157.5	158.3	36.0	1-3	350.7	232.0	38.5	39.6	11.0
c	184	353.3	119.0	121.3	113.0	3-4	352.2	257.4	25.4	26.5	14.5
3	184	351.8	175.8	176.0	0	0-1	350.7	193.6	17.8	18.9	10.1

 TABLE IV
 THE REACTIONS $x C_2H_6 + y H_2$ AT 184°

Expt.	Ratio $C_2H_6:H_2$	Initial pressure, mm.				Time, hrs.	Final pressure, mm.				$-\Delta P_{C_2H_6}$ % per hr.
		Total	C_2H_6	H_2	CH_4		Total	H.C.	$+\Delta H.C.$	$-\Delta H_2$	
1	2:1	267.3	176.2	91.2	0	1.1	301.2	298.6	122.4	88.6	63.2
2a	2:1	264.9	175.4	89.6	0	0.33	236.4	209.0	33.6	62.2	63.7
b	2:1	235.8	141.8	26.8	67.2	.67	264.2
3a	1:2	264.0	87.9	176.1	0	2.0	245.9	102.2	14.3	32.4	8.1
b	1:2	248.3	73.6	146.1	28.6	1.0	247.6	103.8	1.6	2.3	1.8
c	1:2	250.1	72.0	146.3	31.8	3.0	248.1	106.0	2.2	4.2	0.8
4	1:2	269.8	84.5	185.3	0	15.5	268.1	90.0	5.5	7.2	.4
5	3:2	289.0	174.7	114.3	0	0.5	289.5	182.8	8.1	7.6	9.2
6	3:2	290.6	175.8	114.8	0	.5	289.4	182.7	6.9	8.1	7.9
7	2:1	263.2	176.1	87.1	0	.33	262.8	184.1	8.0	8.4	15.2

action proceeds is real and is to be ascribed to the reasonable assumption that hydrogen is strongly adsorbed but the hydrocarbons only weakly. As the hydrogen is consumed more of the surface becomes accessible to activated adsorption of the hydrocarbons. This conclusion is supported by the following data with varying ratios of hydrogen to ethane. The concordance between the data of the two columns $+\Delta H.C.$ and $-\Delta H_2$ save in expt. 1a indicates also the absence of any side reactions, which is not true with other ratios of reactants (*vide infra*). The apparent activation energy of the reactants calculated from the data at the two temperatures gives $E_{app.} \sim 43$ kcal.

In Table IV are recorded experiments with $1C_2H_6 + 0.5 H_2$, $1C_2H_6 + 2H_2$ and $1C_2H_6 + 0.69H_2$.

All the experiments recorded in this Table IV were done successively on one catalyst. The comparison of expts. 1 and 2 with a gas ratio of $2C_2H_6:1H_2$ with expts. 2 and 3 of Table III where the ratio is 1:1 indicates that increase of hydrogen ratio severely reduces the reaction rate. Calculations from the data 2a and 3a of Table III and 1 and 2 of Table IV and from the data of expts. 5,

6, 7 of this latter table would indicate an effect of hydrogen proportional to $\sim P_{H_2}^{-2.5}$. We shall discuss this later. Comparison of expts. 1 and 2 of Table IV with the subsequent experiments of this table at other ratios indicates that during expts. 1 and 2 the nickel catalyst suffered a considerable degree of poisoning leading to abnormally low conversions in expts. 3-7. A critical analysis of the data of the table reveals that the poisoning is due to carbon deposition. In addition to the reaction forming methane (1) $C_2H_6 + H_2 = 2CH_4$ there are occurring simultaneously reactions which may be represented by the over-all equations (2) $2C_2H_6 = C + 3CH_4$ and (3) $C + 2H_2 = CH_4$. These conclusions may be reached especially from a comparison of the columns recording initial and final pressures, *i. e.*, ΔP_{total} and those recording increase of hydrocarbon $+\Delta H.C.$ and decrease of hydrogen pressure $-\Delta H_2$. Thus, in expt. 1a of Table IV, the recovered gas exceeds the amount introduced by 33.9 mm. and the increase in hydrocarbon is 122.4 mm. The increase of hydrocarbon due to reaction (1) with hydrogen is not less than 88.6 mm., which leaves $122.4 - 88.6 =$

TABLE V
 DECOMPOSITION OF ETHANE ON NICKEL AT 218°

Expt.	Initial $P_{C_2H_6}$, mm.	Time, hrs.	Final pressure, mm.				C_2H_6	CO_2 from combustion of C_2H_6 fraction		
			Total	$+\Delta P$	H.C.	$+\Delta H.C.$				
1a	169.4	10.3	186.2	16.8	184.9	15.5	1.3	50.7	136.2	260.5
b	159.7	57	184.6	24.9	183.4	23.7	1.3	76.4	108.5	205.3

33.8 mm. increase coming from reaction (2). This corresponds to a decomposition according to (2) of 67.6 mm. ethane, and therefore to carbon deposition on the surface equivalent to ~ 33.8 mm. In expt. 2a the recovered gas is less than the initial by 28.5 mm. Of the hydrogen consumed some 57 mm. must have reacted in the main with the previously deposited carbon to give 28.5 mm. methane. This leaves only 5.2 mm. hydrogen to react with an equivalent of ethane to give a further 10.4 mm. methane. This would give a total increase of hydrocarbon of $28.5 + 5.2 = 33.7$ mm. to be compared with the observed hydrocarbon increase of 33.6 mm. Expt. 2b appears to repeat 1 since the carbon laid on the surface in expt. 1a was more than 90% consumed by hydrogen in 2a. Similar variations in the nature of the important reaction with change in the carbon-hydrogen ratio of the reaction mixture and change in carbon content of the surface may be traced through the results of expts. 2b-7. It emerges that, in a catalyst heavily charged with carbon, reaction (3) between carbon and hydrogen occurs preferentially to reaction (1). A certain amount of the carbon, however, appears to be laid down in such a form that subsequent reaction does not readily occur. Also, the activity of the catalyst falls steadily due to the deposition of the carbon.

The experiments presented in Table V are concerned with the decomposition of ethane alone on the same nickel catalyst at 218°. The catalyst after evacuation was washed with ethane at 218° for one and a half hours and then evacuated for one hour further. The three final columns of the table give the data obtained by a fractional separation of the hydrocarbon product and a combustion of the ethane fraction to carbon dioxide as a check on its composition.

The fact that the methane formed is, in each case, equal to three times the increase in pressure due to reaction or equal to three times the increase in hydrocarbon plus twice that of the hydrogen, is indicative of the over-all reaction (2) $2C_2H_6 = C + 3CH_4$. The methane yields from the fractionation of the product further confirm this view. The carbon deposited on the catalyst by reason of

this reaction can be removed in part by reaction with hydrogen as indicated in the two experiments of Table VI.

 TABLE VI
 INTERACTION OF HYDROGEN WITH CARBON DEPOSITED ON NICKEL AT 218°

Expt.	P_{H_2} , mm.	Time, hrs.	Recovered gas, mm.			CH_4 by fractiona- tion	
			$-\Delta P$	$+\Delta H.C.$	$-\Delta H_2$		
1a	416.1	4.5	356.0	60.1	57.1	117.2	56.7
b	421.0	14.0	414.4	6.6	6.0	12.6	..

Since $-\Delta H_2$ is twice ($-\Delta P$) or twice ($+\Delta H.C.$) it follows that the hydrocarbon formed is all methane. This was confirmed in the first case by fractionation. The total methane produced amounts to 63.1 mm. equivalent to 42 mm. of C_2H_6 . Some carbon is left on the catalyst and a subsequent measurement of reaction rate with $1C_2H_6:1H_2$ gave very low activity, *i. e.*, 0.9% per hour at 184°.

The Activation Energy of the Reactions of Ethane with Hydrogen and Deuterium to Form Methane and Methane-*d*.—To check the apparently high activation energy deduced from the data of Table III and to obtain comparison between the rates of reaction of hydrogen and deuterium with ethane the data of Table VII were obtained on a new catalyst containing 2 g. of nickel. Again the static method was employed and the experiments with deuterium were interposed between two experiments with hydrogen under comparable conditions.

 TABLE VII
 REACTION OF ETHANE WITH HYDROGEN AND WITH DEUTERIUM TO FORM METHANE

Expt.	Initial volumes, cc.—			Temp., °C.	Time, hrs.	Conversion % C_2H_6
	C_2H_6	H_2	D_2			
28	20.0	20.0		184	1.0	53.7
29	20.1	20.1		172	2.5	28.3
30	20.3		19.4	172	2.5	16.7
31	20.3	19.7		172	2.5	23.9
32	20.3	20.4		157	10.0	21.2
33	20.3		20.9	157	10.0	10.3
34	20.3	21.4		157	10.3	17.5

A slow deterioration of the catalyst with successive experiments does not obscure the obvious result that reaction with deuterium is slower than that with hydrogen. Nor is it serious enough to

prevent the conclusion that the activation energy has the high value previously indicated. The data at 157 and 172° in this table indicate an observed activation energy of ~ 42 kcal. The relative rates of the hydrogen and deuterium reactions at the two temperatures 157 and 172° can be accounted for on the basis of a difference in activation energies of ~ 450 cal.

General Discussion

From these studies of reactivity of ethane-hydrogen mixtures on nickel in the temperature range 157–300°, we conclude that, in the presence of excess hydrogen, the ethane undergoes a dissociative adsorption to methyls which are converted quantitatively with adsorbed hydrogen to methane. With deficiency of hydrogen the activated adsorption of ethane continues beyond the stage of formation of adsorbed methyls at the surface and the dissociative adsorption proceeds via CH_2 and CH to C with simultaneous formation of adsorbed atomic hydrogen. Reaction of this latter with adjacent methyls produces methane which then evaporates. In this temperature range the dissociative process to C appears to be practically complete, carbon and methane being the products formed in overwhelmingly preponderant amount. A small amount of hydrogen escapes from the surface as such. Some of the carbon formed goes over into a form in which it is no longer capable of undergoing the reverse reactions of the dissociative processes discussed and acts as a permanent poison to the catalyst. The bulk of the carbon formed in this temperature range is however recoverable by reaction with hydrogen as methane. All these observations are in best agreement with the calculated equilibrium data in such systems. In the system $2\text{C} + 3\text{H}_2 = \text{C}_2\text{H}_6$ this is quite remarkably true since we compute that at 227° partial pressures $P_{\text{C}_2\text{H}_6} = 0.46$, $P_{\text{H}_2} = 0.54$ atm. are in equilibrium with carbon with a total pressure of 1 atm. In contrast to this in the system $\text{C} + 2\text{H}_2 = \text{CH}_4$ at atmospheric pressure the equilibrium partial pressure at 255° is $P_{\text{H}_2} = 0.03$ atm. The necessity for excess hydrogen in the ethane system is thus evident, while with the methane system minimal pressures of hydrogen prevent carbon formation. In the system $\text{C}_2\text{H}_6 = \text{C} + 3\text{CH}_4$ the equilibrium partial pressure at 184° is $P_{\text{C}_2\text{H}_6} = 0.6 \times 10^{-4}$ atm., and in the system $\text{C}_2\text{H}_6 + \text{H}_2 = 2\text{CH}_4$ at the same temperature $P_{\text{C}_2\text{H}_6} = 2 \times 10^{-4}$ atm.

The occurrence of the exchange reaction to yield deuterio-ethanes in a temperature range where dissociative adsorption to yield methyls is unimportant indicates that the dissociative adsorption of ethane to yield ethyl and hydrogen atom is a process of lower activation energy than that of adsorption to yield methyls. The reverse of the ethane-ethyl-hydrogen dissociative process is the final stage in the formation of ethane from ethylene and hydrogen on such catalysts in the low temperature range. In our previous study of the methanes we found an activation energy of 19 kcal. for the dissociative adsorption to methyl and hydrogen. We expect that the corresponding process for ethane might be less than this value.

The high apparent activation energy of the reaction of ethane with hydrogen to yield methane, ~ 43 kcal., is worthy of note especially since the temperature range in which the reaction occurs is not considerably higher than that in which the exchange reaction occurs. We compare this result with the case of methane and deuterium in which $E \sim 28$ kcal. In both cases the retarding influence of hydrogen contributes to the high value. From the earlier work we assess its contribution at ~ 9 kcal. The simplest explanation of the high activation energy in the present work appears to be that it is associated with a somewhat higher energy of activated adsorption involving dissociation of the C-C bond. Sterically we would expect this to be higher than that involving the C-H bond. Further, of the surface free from hydrogen, available to ethane adsorption, a fraction will be occupied by ethane adsorbed by a mechanism involving the C-H dissociation. Such adsorption will cause an increase in the observed activation energy of the ethane-hydrogen reaction as does hydrogen. If we ascribe the difference between the two observed activation energies in the ethane and methane reactions, $43 - 28 = 15$ kcal., to such an effect, we arrive at the reasonable values for the activation energies of dissociative adsorption of ethane, for the C-C bond ~ 19 kcal., and for the C-H bond ~ 15 kcal. Qualitatively such results are entirely consonant with all our data.

One final point for discussion involves the abnormal inhibitory action of hydrogen ($\propto P_{\text{H}_2}^{-2.5}$) which we deduce from the data of Tables III and IV. Such a high power of the hydrogen pressure cannot be explained on the basis of pressure influence on surface occupied by hydrogen mole-

cules. It may, however, be explained as due to the increasing deposition of carbon with decrease in hydrogen concentration and the preferential occurrence of the reaction between hydrogen and the deposited carbon rather than that between ethane and hydrogen. As we have already observed, our experimental data abundantly confirm this preferential reaction and thus account for the abnormal effect of hydrogen concentration. One alternative possibility is that activation involving the C-C bond requires at least two adjacent elementary spaces of catalyst and that this condition at high hydrogen coverage of the surface might be inversely proportional to a higher power of the hydrogen concentration. Further studies in the general field of hydrocarbon-hydrogen reactions are planned to test these points of view.

Summary

1. The exchange reaction between ethane and deuterium on a nickel catalyst takes place in a lower temperature range, 100–130°, than that

required for the interaction to yield methane, 160–300°.

2. The formation of methane by this reaction has been studied kinetically. The surface reaction is inhibited by hydrogen.

3. At low hydrogen concentrations side reactions occur representable by the equations $2C_2H_6 = C + 3CH_4$ and $C + 2H_2 = CH_4$ and these may become the predominant reactions.

4. The activation energy of the reaction on nickel between ethane and hydrogen to form methane is ~43 kcal. The reaction with deuterium is somewhat slower with an activation energy ~0.5 kcal. higher.

5. An interpretation of these data in terms of a dissociative activated adsorption of ethane is given, leading to the conclusion that the activation energy of dissociative adsorption at the C-C bond is greater than that of the C-H bond.

6. A method of preparation of ethane- d_6 has been described.

PRINCETON, N. J.

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[CONTRIBUTION NO. 142 FROM THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY, RESEARCH LABORATORY OF ORGANIC CHEMISTRY]

Studies in the Urea Series. XIII.¹ Alkyl-nitroureas and Alkyl-nitrobiurets

BY TENNEY L. DAVIS AND NICHOLAS D. CONSTAN

Experiments reported in the tenth paper of this series led to the conclusion that "only those alkylguanidines which contain an unsubstituted amino group form nitro-compounds by direct nitration, the nitro group entering the non-alkylated amino group." A similar generalization is evidently not valid for the alkylureas, for Degner and von Pechmann² have reported that N-nitro-N-methylurea is produced by the nitration of methylurea with ethyl nitrate and concentrated sulfuric acid. Thiele and Lachmann³ on the other hand reported somewhat earlier that ethylurea yields N-nitro-N'-ethylurea by a similar procedure. We have wished to verify this difference between methyl- and ethylurea and to determine in general the be-

havior of the alkylureas on nitration and have carried the study farther to the nitration of two ω -substituted biurets and to the preparation from one of the resulting nitro compounds of certain ω, ω, ω' -trisubstituted biurets.

The nitrate of methylurea on treatment with concd. sulfuric acid yields N-nitro-N-methylurea in which the nitro and methyl groups are both attached to the same nitrogen atom, as is demonstrated by the fact that it yields methylnitramine and urea when treated with ammonia. The nitrates of ethyl-, *n*-propyl- and *n*-butylurea on treatment with concd. sulfuric acid yield alkyl-nitroureas in which the nitro group and the alkyl group are attached to different nitrogen atoms. Unlike methylurea they behave in the same manner as the corresponding alkylguanidines. The structure of the N-nitro-N'-alkylureas is demonstrated by the facts that with ammonia water they yield the alkylureas and with aniline the N-phenyl-N'-alkylureas. As would be expected they rearrange somewhat less readily than nitro-

(1) Earlier papers of this series: I, Davis and Underwood, *THIS JOURNAL*, **44**, 2595 (1922); II, VI, VII, VIII, Davis and Blanchard, *ibid.*, **45**, 1816 (1923); **51**, 1790, 1801, 1806 (1929); III, Davis, *Proc. Nat. Acad. Sci.*, **11**, 68 (1925); IV, Davis and Abrams, *Proc. Am. Acad. Arts, Sci.*, **61**, 437 (1926); V, Davis and Luce, *THIS JOURNAL*, **49**, 2303 (1927); IX, X, Davis and Elderfield, *ibid.*, **54**, 1499 (1932); **55**, 731 (1933); XI, Davis and Farnum, *ibid.*, **56**, 883 (1934); XII, Davis and Ebersole, *ibid.*, **36**, 885 (1934).

(2) Degner and von Pechmann, *Ber.*, **30**, 652 (1897).

(3) Thiele and Lachmann, *Ann.*, **288**, 285 (1895).